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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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(54) Title: MOLECULAR-LEVEL THERMAL-MANAGEMENT MATERIALS COMPRISING SINGLE-WALL CARBON NANOTUBES

(57) Abstract: The present invention relates to devices, processes and materials comprising single-wall carbon nanotubes wherein the single-wall carbon nanotubes serve to transport heat to or from a nanometer scale region wherein that heat is generated or dissipated. Because of their small physical size, excellent heat conductivity, and relatively large surface area, single-wall carbon nanotubes are novel in their function as nanometer-scale agents for heat transport. Appropriately configured in association with a source of heat such as the catalyst for an exothermic polymerization reaction, single wall carbon nanotubes can effectively conduct heat away from the reaction site. This thermal management on a molecular level enables a new class of materials and processes in all areas where heat transport is important. Additionally, new materials such as improved polymer compositions are produced by processes that are thermally-managed at the molecular level by the objects of this invention.

MOLECULAR-LEVEL THERMAL-MANAGEMENT MATERIALS COMPRISING SINGLE-WALL CARBON NANOTUBES

This application claims priority from U.S. provisional application 60/358,876, filed on February 22, 2002, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

This invention relates to devices, materials, and processes comprising single-wall carbon nanotubes wherein the single-wall carbon nanotubes serve to transport heat to or from a nanometer scale region wherein that heat is generated or dissipated. Single-wall carbon nanotubes (SWNT), commonly known as "buckytubes," have been the subject of intense research since their discovery due to their unique properties, including high strength, stiffness, and thermal and electrical conductivity. SWNT are fullerenes consisting essentially of sp^2-hybridized carbon atoms typically arranged in hexagons and pentagons. For background information on single-wall carbon nanotubes, see B.I. Yakobson and R. E. Smalley, *American Scientist*, Vol. 85, July-August, 1997, pp. 324-337. Multi-wall carbon nanotubes are nested single-wall carbon cylinders and possess some properties similar to single-wall carbon nanotubes. However, since single-wall carbon nanotubes have fewer defects than multi-wall carbon nanotubes, the single-wall carbon nanotubes are generally stronger and more conductive, both thermally and electrically. Additionally, single-wall carbon nanotubes have considerably higher available surface area per gram of carbon than multi-wall carbon nanotubes.

In many electrical, chemical and physical processes, heat is generated or required in nanometer-scale regions, often by molecular-level interactions of a chemical or physical nature. In circumstances where heat is generated, that heat often has detrimental effects and must be removed from the process. In processes where heat is required, it is most preferable that the heat be delivered at a precise location on a molecular scale, but that, heretofore, has generally been impossible. Even though heat is generated or required by specific molecular-level interactions, the transport of heat in most chemical and physical processes is provided through its transport in bulk materials. Therefore, it is anticipated that the art of chemical and physical processes will be advanced by an invention that enables enhanced transport of heat generated or required in molecular-level interactions, particularly if those means operate at the nanometer scale.

SUMMARY OF THE INVENTION

This invention relates to devices, materials, and processes that incorporate single-wall carbon nanotubes as heat transfer agents to improve the efficacy of heat transport to and from nanometer-scale regions. A nanometer-scale region, for the purposes of this invention, is one contained within a sphere of 30 nanometers in diameter, more preferably 10 nanometers in diameter, and most preferably 3 nanometers in diameter. Said nanometer-scale region can contain either a heat source or a heat sink. Molecular-level processes that act as heat sources or heat sinks occur within such nanometer-scale regions. If a portion of one or more single-wall carbon nanotubes lies within this nanometer-scale region, it can dispense or absorb heat there and effectively transport heat to or from that region. This invention enables a new level of heat transfer engineering in many bulk-scale chemical and physical processes, by providing for thermal management at the molecular level.

One embodiment of the invention is a molecular level thermal management device comprising at least one single wall carbon nanotube. In this device, at least some portion of a single-wall carbon nanotube shares a nanometer-scale region with a heat source, the single-wall carbon nanotube is in contact with an environment to which it can transfer heat, and the single-wall carbon nanotube transfers heat from the heat source to said environment.

Another embodiment of the invention is a molecular level thermal management device comprising at least one single wall carbon nanotube. In this device, at least some portion of a single-wall carbon nanotube shares a nanometer-scale region with a heat sink, the single-wall carbon nanotube is in contact with an environment from which it can receive heat, and the single-wall carbon nanotube transfers heat from said environment to the heat sink.

Another embodiment of the invention is a polymerization catalyst system that comprises a polymerization catalyst and a plurality of single-wall carbon nanotubes. Additional embodiments are a polymerization process, wherein at least one monomer is polymerized in the presence of the catalyst system, and the polymer produced by that process.

Another embodiment of the invention is a fixed-bed polymerization reactor. The reactor comprises at least one fixed-bed that comprises at least one polymerization catalyst attached to single-wall carbon nanotubes. The nanotubes are formed into a macroscopic porous structure, which allows diffusion of at least one monomer to an active polymerization site on the polymerization catalyst and transport of at least one polymer and heat away from the active site and out of the fixed-bed.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

Various embodiments of this invention use single-wall carbon nanotubes to enable transport of heat to or from a nanometer scale region. Implementation of this nanometer-scale heat transport enables new devices, materials, and processes.

For clarity in the following description, however, this invention will initially be discussed with respect to an embodiment where single-wall carbon nanotubes serve to remove heat from a nanometer-scale region where the heat is being produced. In this embodiment, some portions of single-wall carbon nanotubes are placed in close proximity to the region of heat generation, and other portions of said nanotubes lie between that region and an environment that enables removal of heat from the single-wall carbon nanotube surface. In this embodiment, single-wall carbon nanotubes are molecular-level heat transfer conduits that enable heat removal from heat-generating molecular-level processes. Single-wall carbon nanotubes are individual molecules that are excellent conductors of heat. The small physical size of single-wall carbon nanotubes permits portions of them to be located in contact with or in very close proximity to the heat source. Heat from the source can be transferred to the single-wall carbon nanotubes through any of the known means of thermal energy transfer, including, but not limited to, convection, radiation, vibrational energy transfer, electronic energy transfer, mass transfer and accommodation, molecular heat conduction, and combinations thereof. Upon receiving the heat energy within the nanometer-scale region, the single-wall carbon nanotubes will then efficiently conduct heat away from the nanometer-scale region and distribute that heat over the single-wall carbon nanotube surface. If that surface is in an environment where heat can be removed from that surface, then the locally-generated heat will be effectively dissipated, and the temperature at the heat-generation region will be lowered. The environment for heat removal is one that allows transfer of heat from the single-wall carbon nanotube surface by any of the known means of thermal energy transfer, including, but not limited to, convection, radiation, vibrational energy transfer, electronic energy transfer, mass transfer and accommodation, molecular heat conduction, and combinations thereof. The device of this invention can comprise more than one single wall carbon nanotube and heat can be transferred from one single-wall carbon nanotube to another as it is transported. Single-wall carbon nanotubes are particularly effective in redistribution of heat because they are nanometer scale structures with excellent thermal conductivity and relatively large surface areas.

One embodiment of the heat-removal device described above is a catalyst system for an exothermic polymerization process. In this embodiment, the catalyst system comprises

single-wall carbon nanotubes and a polymerization catalyst wherein the single-wall carbon nanotubes are directly associated with the catalyst. This association can, without limitation, include physisorption, chemisorption, and/or chemical bonding of the single-wall carbon nanotubes to the catalyst. The chemical bonding can be covalent, ionic or a combination of both, and can occur on the single-wall carbon nanotubes' open ends, closed ends, side walls, defects in the side walls and combinations thereof. This catalyst system composition enables formation of new high-molecular weight polymers, improved polymerization processing methods, and new composite compositions comprising single-wall carbon nanotubes and polymers. During the polymerization process the catalyst participates in an exothermic polymerization reaction forming a polymer material, and the local heat produced in a nanometer-scale region containing the catalyst is carried away by the nanotube material.

Another embodiment of this invention is a material comprising the devices described above. For instance, one can create a bulk composition comprised of single-wall carbon nanotube material combined with entities which serve as a heat sources or sinks. Such a composition could, for instance, be a material comprising single-wall carbon nanotubes with a catalyst that can participate an exothermic chemical reaction.

Another embodiment of this invention is a process utilizing one or more of the devices of this invention, and products of that process. One example would be the polymerization process for polyolefins discussed in Example 1, and products of that process.

This invention admits many variations. In other embodiments, the highly porous nature of single-wall carbon nanotube mats and felts can enable new types of polymerization reactors, such as fixed bed reactors, micro-reactors, catalyst support films, and chemically-active materials comprising the present invention. Suspended single-wall carbon nanotube catalysts with polymers adsorbed on or wrapped around the nanotubes can be left in the polymer material to provide new compositions of polymers reinforced with highly dispersed nanotubes. Because of the intimate proximity of the single-wall carbon nanotube structure to the polymerization site, these materials have enhanced polymer alignment and comprise polymers with molecular weights and mechanical properties enhanced over those produced by other polymerization procedures. Such new compositions will have improved properties such as strength, electrical conductivity and processability into stronger films and fibers. More generally, this invention admits the fabrication of a wide range of materials and devices where thermal management is important on a nanometer scale.

Other examples include providing heat to endothermic reactions wherein the catalytic entity is placed near the end of a single-wall carbon nanotube or bundle of such nanotubes.

Yet other examples include placing one or more single-wall carbon nanotubes with one or more of their ends in proximity to one or more electronic devices (e.g. transistors, diodes, multi-junction devices, resistors, thermistors, sensors, reactive elements, transducers, memory elements, and combinations thereof) in semiconductor electronics assemblies wherein the single-wall carbon nanotubes are added during an appropriate processing step. In this embodiment, the single wall carbon nanotubes carry away heat generated in junctions in the semiconductor assemblies. Another example is in the creation of high-energy materials, such as explosives, rocket fuel and incendiary chemicals where one seeks to control the burning rate by molecular-level thermal management. In other applications for energy-absorbing materials, molecular-level thermal management can provide heat conduction that enables a chemical reaction front to propagate through a material, enabling dissipation of energy in the material. This application of the invention is particularly useful in auto bodies and armor, and other materials designed to absorb energy in a controlled-failure scenario.

In one embodiment, single-wall carbon nanotubes are incorporated in an olefin polymerization catalyst system to provide a more effective catalytic process. Another embodiment of the invention comprises improved polymer compositions generated by such a catalyst system. In one particular embodiment, for example, a device comprises single-wall carbon nanotubes that are configured in proximity to nanometer-scale regions where heat is generated during a process. Here, that configuration can be fabricated by contacting an olefin polymerization catalyst with single-wall carbon nanotubes ends, sides or combinations thereof. Another embodiment of the invention is a material comprising such devices. A further embodiment of the invention is a method that uses said material in a chemical process, such as the production of a polyolefin. Another embodiment of the invention comprises any product of that production process. These products can include polyolefin materials whose properties exceed those of known polyolefin materials in the areas of molecular weight, molecular orientation, strength, toughness, and thermal stability. This method of polyolefin production also naturally produces a material which is a composite of polyolefin polymer and single-wall carbon nanotubes, and that material and the process for its production are also embodiments of this invention.

Olefin polymerization catalysts are known to those skilled in the art of manufacturing polyethylene, polypropylene, polybutenes, polyisobutylenes, polystyrenes and various copolymers, such as ethylene-butene copolymers, ethylene-propylene copolymers and terpolymers, isobutylene-isoprene copolymers (butyl rubber) and other polymers. Such

polymerization catalysts include aluminum, magnesium and titanium halides, conventional Ziegler-Natta, newer metallocene and other "single-site" catalysts such as zirconium- and titanium-based metallocenes with alumoxane or other non-coordinating anionic co-catalysts, such as perfluorophenyl borane compounds.

Association of chemical entities with single-wall carbon nanotubes can be done by means known to those skilled in the art. Examples of association include chemical bonding, van der Waals interactive forces, polar interactions, and indirect contact through other materials.

Incorporation of single-wall carbon nanotubes in olefin polymerization catalyst systems provides an improved catalyst composition that has functionality previously unknown in olefin polymerization catalysts. This functionality derives from the ability of the single-wall carbon nanotubes to receive and transfer heat away from the point at which the polymerization reaction is occurring. Additionally this invention includes a composition of matter comprising association of a catalytic moiety (such as an olefin polymerization catalyst) with one or more single-wall carbon nanotubes that serve as a "molecular-level heat transfer agent".

Olefin polymerization is a highly exothermic reaction. The heat generated when the monomer reacts with the catalyst and is inserted into the growing polymer chain must be transferred away from the catalyst site. If this is not done, a runaway reaction can result as the catalyst heats up and the reaction proceeds faster releasing more heat. To control heat generation, catalysts and reactor systems are designed to limit the rate of polymerization. In addition, local heating at the catalyst site can cause limitations in the molecular weight of the polymers made because, at elevated temperatures, the rates of termination reactions increase in comparison to the rates for propagation (chain growth) reactions. Furthermore, local heating can cause catalyst deactivation. By conducting heat away from the catalyst site, the single-wall carbon nanotubes will allow higher molecular weight polymers to be made at faster rates and with less catalyst deactivation. Additionally, the enhanced molecular-level thermal management provided by the catalyst composition described here helps ensure a more uniform temperature throughout the polymerization section of the reactor and mitigates against formation of "runaway hot spots" in the reactor where polymer growth termination and unwanted catalyst deactivation can occur.

The preceding description of specific embodiments of the present invention is not intended to be a complete list of every possible embodiment of the invention. Persons skilled

in this field will recognize that modifications can be made to the specific embodiments described here that would be within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A molecular level thermal management device comprising at least one single wall carbon nanotube, wherein:

   at least some portion of a single-wall carbon nanotube shares a nanometer-scale region with a heat source,

   the single-wall carbon nanotube is in contact with an environment to which it can transfer heat, and

   the single-wall carbon nanotube transfers heat from the heat source to said environment.

2. The device of claim 1, wherein the single-wall carbon nanotube is in contact with the heat source.

3. The device of claim 1, wherein the heat source is a chemical reaction.

4. The device of claim 1, wherein the heat source is an electronic device.

5. The device of claim 1, wherein the device forms part of a fixed-bed reactor, a micro-reactor, a catalyst support structure, or a semiconductor electronic assembly.

6. A material comprising at least one device of claim 1.

7. A molecular level thermal management device comprising at least one single wall carbon nanotube, wherein:

   at least some portion of a single-wall carbon nanotube shares a nanometer-scale region with a heat sink,

   the single-wall carbon nanotube is in contact with an environment from which it can receive heat, and

   the single-wall carbon nanotube transfers heat from said environment to the heat sink.

8. The device of claim 7, wherein the single-wall carbon nanotube is in contact with the heat sink.

9. The device of claim 7, wherein the heat sink is a chemical reaction.

10. The device of claim 7, wherein the heat sink is an electronic device.

11. The device of claim 7, wherein the device forms part of a fixed-bed reactor, a micro-reactor, a catalyst support structure, or a semiconductor electronic assembly.

12. A material comprising at least one device of claim 2.

13. A polymerization catalyst system comprising a polymerization catalyst and a plurality of single-wall carbon nanotubes.

14. The polymerization catalyst system of claim 13, wherein the polymerization catalyst is adapted to catalyze olefin polymerization.

15. A polymerization process, wherein at least one monomer is polymerized in the presence of a catalyst system that comprises a polymerization catalyst and a plurality of single-wall carbon nanotubes.

16. The process of claim 15, wherein the polymerization process forms at least one polyolefin.

17. A polymer produced by polymerization of at least one monomer in the presence of a polymerization catalyst system that comprises a polymerization catalyst and a plurality of single-wall carbon nanotubes.

18. The polymer of claim 17, wherein at least one monomer is an olefin and the polymer is a polyolefin.

19. A high-energy material comprising at least one device according to claim 1, and at least one explosive, rocket fuel, incendiary chemical, or combination thereof.

20. A high-energy material comprising at least one device according to claim 7, and at least one explosive, rocket fuel, incendiary chemical, or combination thereof.

21. A fixed-bed polymerization reactor that comprises at least one fixed-bed that comprises at least one polymerization catalyst attached to single-wall carbon nanotubes which are formed into a macroscopic porous structure which allows diffusion of at least one monomer to an active polymerization site on the polymerization catalyst and transport of at least one polymer and heat away from the active site and out of the fixed-bed.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/05254

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K5/14 C08F4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HAFNER J H ET AL: "CATALYTIC GROWTH OF SINGLE-WALL CARBON NANOTUBES FROM METAL PARTICLES" CHEMICAL PHYSICS LETTERS, NORTH-HOLLAND, AMSTERDAM, NL, vol. 296, no. 1/2, 30 October 1998 (1998-10-30), pages 195-202, XP000869784 ISSN: 0009-2614 page 196 -page 198 ---	13
X	WO 95 10481 A (DU PONT) 20 April 1995 (1995-04-20) the whole document ---	13
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 June 2003	13/06/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Puetz, C

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	YAKOBSON B I ET AL: "FULLERENE NANOTUBES: C1,000,000 AND BEYOND SOME UNUSUAL NEW MOLECULES-LONG, HOLLOW FIBERS WITH TANTALIZING ELECTRONIC AND MECHANICAL PROPERTIES-HAVE JOINED DIAMONDS AND GRAPHITE IN THE CARBON FAMILY" AMERICAN SCIENTIST, NEW HAVEN, CT, US, vol. 85, no. 4, July 1997 (1997-07), pages 324-337, XP001025773 ISSN: 0003-0996 cited in the application page 335, left-hand column ---	7,8,10
P,X	DE 100 48 406 A (INFINEON TECHNOLOGIES AG) 6 June 2002 (2002-06-06) column 1, line 35 -column 2, line 44 column 3, line 35 -column 4, line 14 column 5, line 49 -column 6, line 22 claims 1,8-12,20,21 ---	13
A	EP 1 059 266 A (ILJIN NANOTECH CO LTD ;LEE CHEOL JIN (KR)) 13 December 2000 (2000-12-13) claims 1,2 -----	13

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-21

Present claims 1-16 and 19-21 relate to an extremely large number of possible devices, materials, polymerization catalyst systems and polymerization processes. In fact, the claims contain so many options that a lack of clarity and conciseness within the meaning of Article 6 PCT arises. Furthermore no embodiment has been disclosed in a manner sufficientely clear and complete for a skilled person to reduce the intended technical teaching to practice, at least not without undue burden of experimentation; the application lacks disclosure within the meaning of Article 5 PCT to such an extent that a meaningful search for the numerous claims across their whole breadth is not possible. Consequently, the search has been carried out for those parts of the application which do appear to be clear and concise, namely polymerization catalyst systems, wherein the polymerization catalyst is in contact with single-wall carbon nanotubes and the use of said catalyst systems to catalyze olefin polymerizations (see page 5, line 15 - page 6, line 31). The other stated applications (see page 5, lines 1-14) have been regarded as being merely speculative and not being disclosed and supported by the present application within the sense of Articles 5 and 6 PCT, and thus not searched.

Furthermore no search at all has been performed for claims 17 and 18. These claims for products are only defined in terms of their process of manufacture, without indicating any clear product feature that would enable a meaningful search; moreover said claims lack support and disclosure within the meaning of Articles 6 and 5 PCT to such an extent that a meaningful search is impossible.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

International application No.
PCT/US 03/05254

INTERNATIONAL SEARCH REPORT

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-21
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 03/05254

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9510481 A	20-04-1995	WO 9510481 A1	20-04-1995
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EP 1059266 A	13-12-2000	CN 1277145 A	20-12-2000
		EP 1059266 A2	13-12-2000
		JP 2001020071 A	23-01-2001
		KR 2001049479 A	15-06-2001
		US 6350488 B1	26-02-2002

Form PCT/ISA/210 (patent family annex) (July 1992)